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(19)

(54) IMPROVEMENTS IN THERMOPLASTIC COMPOSITIONS OF POLY(1,4-BUTYLENE)TEREPHTHALATE RESIN AND IONICALLY CROSSLINKED COPOLYMERS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides a thermoplastic composition that is based on the combination of poly (1,4-butylene terephthalate) resin and an ionically crosslinked copolymer of an α-olefin and an α,β-ethylenically unsaturated mono- or dicarboxylic acid.

High molecular weight linear polyesters and copolyesters of terephthalic and isophthalic acid are well known in the prior art. These polymers are described in the literature and particular reference is made to U.S. 2,465,319 and U.S. 3,047,539.

While these materials have many desirable properties which make them useful for diverse applications, it is desirable for certain applications to increase the elongation properties while not adversely affecting the impact strength, heat distortion temperature or other critical properties of the linear polyester molding compositions.

It has now been found that the addition of preferably a minor amount of an ionically crosslinked copolymer of an α-olefin and an α,β-ethylenically unsaturated mono- or dicarboxylic acid to a linear polyester molding composition will dramatically increase the elongation to break characteristics of said linear polyester molding composition. This increase in the elongation of the polyester is achieved without materially affecting the physical properties of the polyester resin. In addition to the increase in elongation, a surprising increase in melt viscosity is achieved by the compositions of the invention as compared with linear polyester resins that are unmodified with ionically crosslinked copolymers. This increase in melt viscosity extends the usefulness of the linear polyesters to certain blow molding applications that require a high melt viscosity.

This phenomena has not been observed in linear polyesters that have been modified with α-olefin-monocarboxylic acid copolymers that have been ionically crosslinked with zinc ions.

The thermoplastic molding composition of the present invention will comprise:

(a) a high molecular weight poly(1,4-butylene)terephthalate resin; and

(b) an ionically crosslinked copolymer containing, based on the polymer weight, at least 50 mol % of residues of α-olefins having the general formula $RCH{=}CH_2$ where R is a radical selected from hydrogen and alkyl radicals having from 1 to 8 carbon atoms, and 0.2 to 25 mol % of residues of an α,β-ethylenically unsaturated monocarboxylic or dicarboxylic acid, said copolymer containing uniformly distributed throughout a metal ion having a valence of 1 to 3 inclusive, selected from Na^+, K^+, Li^+, Cs^+, Ag^+, Hg^+, Cu^+, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Cu^{+2}, Cd^{+2}, Hg^{+2}, Sn^{+2}, Pb^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Al^{+3}, Se^{+3} and Y^{+3}, wherein at least 10 percent of the carboxylic acid groups being neutralized by the said metal ions.

Also included within the scope of the material poly(1,4-butylene

terephthalate) resin, hereinafter referred as the polyester resin are the branched copolyesters of poly(1,4-butylene terephthalate).

These copolyesters are branched either by crosslinking through chemical linkages or by other known methods. They may contain minor amounts of, e.g., from 0.5 to 15 mole percent of the total 1,4-butylene units, of other aliphatic linkages, e.g., those of from 2 to 10 carbon atoms, such as dimethylene, trimethylene, hexamethylene and decamethylene linkages as well as cycloaliphatic, e.g., 1,4-dimethylene-cyclohexane linkages. In addition to the terephthalic acid units, other dicarboxylic acid units, such as adipic, naphthalene dicarboxylic, isophthalic and orthophthalic units may be present in small amounts, e.g., from 0.5 to 15 mole percent of the total acid units.

Especially useful are branched high melt viscosity poly(1,4-butylene terephthalate) resins, which include a small amount of a branching component containing at least three ester forming groups. The branching component can be one which provides branching in the acid unit portion of the polyester, or in the glycol unit portion, or it can be a hybrid. Illustrative of such branching components are tri- or tetracarboxylic acids, such as trimesic acids, pyromellitic acid and lower alkyl esters thereof, or, preferably, polyols, and especially preferably, tetrols, such as pentaerythritol; triols such as trimethylolpropane; or dihydroxy carboxylic acids and hydroxydicarboxylic acids and derivatives, such as dimethyl hydroxyterephthalate.

The relative amount of branching component can vary, but is always kept at a minor proportion, e.g., of up to 5 mole percent maximum, for every 100 moles of the terephthalate units in the branched polyester. Preferably, the range of branching component included in the esterification mixture (and generally, that included in the product), will be from 0.01 to 3 mole percent based on the terephthalate units. Especially preferably, it will comprise from 0.02 to 1 mole percent, based on the terephthalate component.

As already stated, the ionic copolymers comprise a polymer of an α-olefin having the general formula $RCH=CH_2$ wherein R is hydrogen or an alkyl radical having from 1 to 8 carbon atoms inclusive, the olefin content of said polymer being at least 50 mole percent based on the polymer, and an α,β-ethylenically unsaturated mono- or dicarboxylic acid having from 3 to 8 carbon atoms, the acid monomer content of said polymer being from 0.2 to 25 mole percent based on the polymer, said polymer containing a metal ion selected from the group consisting of ions of alkali metals and alkaline earth metals uniformly distributed through the polymer in sufficient quantity to neutralize at least 10 percent of said carboxylic acid monomer.

The preferred alkali metal ion is Na^+, although K^+ and Li^+ ions may be employed. Preferred polymers will employ ethylene as the α-olefin and acrylic or methacrylic acid as the α,β-ethylenically unsaturated carboxylic acid monomer.

The ionically cross-linked polymer components can be made by known methods and they are available commercially. They are described in the Encyclopedia of Polymer Science and Technology, John Wiley & Sons, Inc., New York, Volume 6, 1967, pages 420—431, and in references cited therein. They are also described in Modern Plastics Encyclopedia, McGraw-Hill, Co., New York, Volume 51, No. 10A, October 1974, pages 40 and 49. In general, they are transparent, moldable resins having a specific gravity of 0.93—0.96 g./cc., a specific volume of 30.0—29.0 cu. in./lb., a Shore D hardness, when molded, of 50—65, a volume resistivity of $> 10^{18}$ ohm-cm; a refractive index of about 1.51 and excellent resistance to attack by alkalis and organic solvents. They are commercially available from the duPont Company under the trade name Surlyn (Registered Trade Mark) Ionomers.

The ionically cross-linked polymer components useful in this invention can be made following the teachings of Canadian Patent No. 674,595. In one illustrative procedure, 300 g. of an ethylene/methacrylic acid copolymer containing 10 wt.% of methacrylic acid is milled at 150°C. and then 24 g. of sodium methoxide in 100 ml. of methanol is worked into the hot copolymer. The mixture is worked for an additional 15 minutes, during which time the initially soft, fluid melt becomes stiff and rubbery. It is sheeted off, cooled and comminuted for use. The other materials within the scope of the above-defined family can be obtained in a like manner by substituting appropriate copolymers, and strontium hydroxide, magnesium acetate, sodium hydroxide, tc. for the sodium methoxide. Instead of using copolymers formed from the monom rs, grafts of acrylic acid, for example, onto polypropylene r polyethylene, can also be substituted.

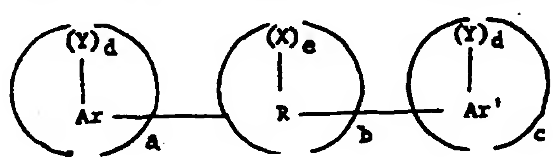
Th compositions of the invention will preferably comprise from 95 to 99.9 parts by weight of the linear polyester resin and from 5 to 0.1 parts by weight of the ionically cross-linked copolymer. The preferred compositions will include from 99 to 98.8 parts by weight of the linear polyester and from 0.2 to 1 part by weight of the ionically cross-linked copolymer.

The compositions of the present inv ntion also preferably include flame retardant agents that render the compositions flam retardant. Usable flame retardants are disclosed in U.S. 3,833,685, U.S. 3,341,154 and U.S. 3,671,487. Other flame retardants are disclosed in U.S. 3,681,281, U.S. 3,557,053, U.S. 3,830,771 and U.K. 1,358,080.

In general, the flame-retardant additives useful in this invention comprise a family of chemical compounds well known to those skilled in the art. Generally speaking, the more important of these compounds contain chemical elements employed for their ability to impart flame resistance, e.g., bromine, chlorine, antimony, phosphorus and nitrogen. It is preferred that the flame retardant additive comprises a halogenated organic compound (brominated or chlorinated); a halogen-containing organic compound in admixture with antimony oxide; elemental phosphorus or a phosphorus compound; a halogen-containing compound in admixture with a phosphorus compound or compounds containing phosphorus-nitrogen bonds or a mixture of two or more of the foregoing.

The amount of flame-retardant additive used is not critical to the invention, so long as it is present in a minor proportion based on said composition — major proportions will detract from physical properties — but at least sufficient to render the polyester resin non-burning or self-extinguishing. Those skilled in the art are well aware that the amount will vary with the nature of the resin and with the efficiency of the additive. In general, however, the amount of additive will be from 0.5 to 50 parts by weight per hundred parts of resin. A preferred range will be from 3 to 25 parts and an especially preferred range will be from 8 to 12 parts of additive per 100 parts of resin. Smaller amounts of compounds highly concentrated in the elements responsible for flame-retardance will be sufficient, e.g., elemental red phosphorus will be preferred at 0.5 to 2.0 parts by weight per hundred parts of resin, while phosphorus in the form of triphenyl phosphate will be used at 25 parts of phosphate per 100 parts of resin, and so forth. Halogenated aromatics will be used at 8 to 12 parts and synergists, e.g., antimony oxide will be used at about 2 to 5 parts by weight per 100 parts of resin.

Among the useful halogen-containing compounds are those of the formula:



wherein R is an alkylene, alkylidene or cycloaliphatic linkage, e.g., methylene, ethylene, propylene, isopropylene, isopropylidene, butylene, isobutylene, amylene, cyclohexylene, cyclopentylidene, and the like; a linkage selected from ether; carbonyl; amine; a sulfur containing linkage, e.g., sulfide, sulfoxide, sulfone; a phosphorus-containing linkage, and the like. R can also consist of two or more alkylene or alkylidene linkages connected by such groups as aromatic, amino, ether, carbonyl, sulfide, sulfoxide, sulfone and a phosphorus-containing linkage. Other groups which are represented by R will occur to those skilled in the art.

Ar and Ar' are mono- or polycarbocyclic aromatic groups such as phenylene, biphenylene, terephenylene, naphthylene, and the like. Ar and Ar' may be the same or different.

Y is a substituent selected from organic, inorganic, or organometallic radicals. The substituents represented by Y include (1) halogen, e.g., chlorine, bromine, iodine, or fluorine or (2) ether groups of the general formula OE, wherein E is a monovalent hydrocarbon radical similar to X or (3) monovalent hydrocarbon groups of the type represented by R or (4) other substituents, e.g., nitro and cyano, said substituents being essentially inert provided there be at least one and preferably two halogen atoms per aryl, e.g., phenyl nucleus.

X is a monovalent hydrocarbon group exemplified by the following: alkyl, such as methyl, ethyl, propyl, isopropyl, butyl and decyl, aryl groups such as phenyl, naphthyl, biphenyl, xylyl, tolyl, and the like; aralkyl groups, such as benzyl,

ethylphenyl, and the like; cycloaliphatic groups such as cyclopentyl and cyclohexyl, as well as monovalent hydrocarbon groups containing inert substituents therein. It will be understood that where more than one X is used they may be alike or different.

The lett r *d* represents a whole number ranging from 1 t a maximum equivalent to the number of replaceable hydrogens substituted on the aromatic rings comprising Ar or Ar'. The letter *e* represents a whole number ranging from 0 to a maximum controlled by the number of replaceable hydrogens on R. The letters *a*, *b* and *c* represent whole numbers including 0. When b is not 0, neither a nor c may be 0. Otherwise either a or c, but not both, may be 0. Where b is 0, the aromatic groups are joined by a direct carbon-carbon bond.

The hydroxyl and Y substituents on the aromatic groups, Ar and Ar' can be varied in the ortho, meta or para positions on the aromatic rings and the groups can be in any possible geometric relationship with respect to one another.

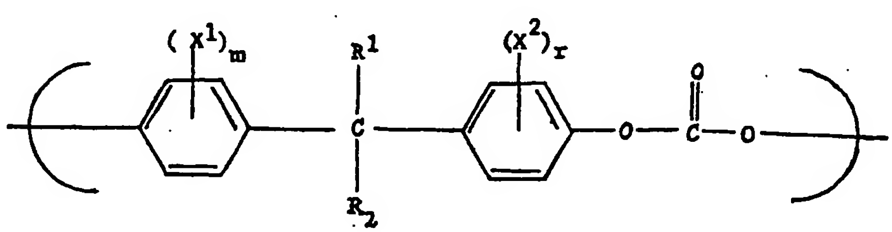
Included within the scope of the above formula are biphenyls of which the following are representative:

2,2-bis-(3,5-dichlorophenyl)propane
bis-(2-chlorophenyl)methane
bis-(2,6-dibromophenyl)methane
1,1-bis-(4-iodophenyl)ethane
1,2-bis-(2,6-dichlorophenyl)ethane
1,1-bis-(2-chloro-4-iodophenyl)ethane
1,1-bis-(2-chloro-4-methylphenyl)ethane
1,1-bis-(3,5-dichorophenyl)ethane
2,2-bis-(3-phenyl-4-bromophenyl)ethane
2,6-bis-(4,6-dichloronaphthyl)propane
2,2-bis-(2,6-dichlorophenyl)pentane
2,2-bis-(3,5-dichromophenyl)hexane
bis-(4-chlorophenyl)phenylmethane
bis-(3,5-dichlorophenyl)cyclohexylmethane
bis-(3-nitro-4-bromophenyl)methane
bis-(4-hydroxy-2,6-dichloro-3-methoxyphenyl)methane
2,2-bis-(3,5-dichloro-4-hydroxyphenyl)propane and
2,2-bis-(3-bromo-4-hydroxyphenyl)propane

The preparation of these and other applicable biphenyls are known in the art. In place of the divalent aliphatic group in the above examples may be substituted sulfide and sulfoxy.

Included within the above structural formula are substituted benzenes exemplified by 1,3-dichlorobenzene, 1,4-dibromobenzene, 1,3-dichloro-4-hydroxybenzene, hexyachlorobenzene, hexabromobenzene, and biphenyls such as 2,2'-dichlorobiphenyl, 2,4'-dibromobiphenyl, and 2,4'-dichlorobiphenyl.

Aromatic carbonate homopolymers having repeating units of the formula:



wherein R^1 and R^2 are hydrogen, (lower)alkyl or phenyl, X^1 and X^2 are bromo or chloro and *m* and *r* are from 1 to 4. These materials may be prepared by techniques well known to those skilled in the art.

Also aromatic carbonate copolymers in which from 25 to 75 wt. percent of the repeating units comprise chloro- or bromo-substituted dihydric phenol, glycol or dicarboxylic acid units.

The preferred halogen compounds for this invention are aromatic halogen compounds such as halogenated polycarbonates, chlorinated benzene, brominated benzene, chlorinated biphenyl, brominated terphenyl, or a compound comprising two phenyl radicals separated by a divalent alkylene or oxygen group and having at least two chlorine or bromine atoms per phenyl nucleus, and mixtures of at least two of the foregoing.

Especially preferred are the halogenated polycarbonates either, alone, or mixed with antimony oxide.

In general, the preferred phosphate compounds are selected from elemental ph sphorus or organic phosphonic acids, phosphonates, phosphinates, phosphonites, phosphinites, phosphene oxides, phosphenes, phosphites or phosphates. Illustrative are triphenyl phosphene oxide. This can be used alone or mixed with hexabromobenzene or a chlorinated biphenyl and, optionally, antimony oxide.

Typical of the preferred phosphorus compounds to be employed in this invention would be those having the general formula:

$$\begin{array}{c} O \\ \| \\ QO—P—OQ \\ | \\ OQ \end{array}$$

where each Q represents the same of different radicals including hydrocarbon radicals such as alkyl, cycloalkyl, aryl, alkyl substituted aryl and aryl substituted alkyl; halogen; hydrogen and combinations thereof provided that at least one of said R's is aryl. Typical examples of suitable phosphates include, phenylbisdodecyl phosphate, phenylbisneopentyl phosphate, phenylethylene hydrogen phosphate, phenyl-bis-(3,5,5'-trimethylhexyl phosphate), ethyldiphenyl phosphate, 2-ethylhexyl di(p-tolyl)phosphate, diphenyl hydrogen phosphate, bis(2-ethylhexyl) p-tolylphosphate, tritolyl phosphate, bis(2-ethylehexyl)phenyl phosphate, tri(nonyl-phenyl)phosphate, phenylmethyl hydrogen phosphate, di(dodecyl) p-tolyl phosphate, tricresyl phosphate, triphenyl phosphate, dibutylphenyl phosphate, 2-chloroethyldephenyl phosphate, p-tolyl bis(2,5,5'-trimethylhexyl)phosphate, 2-ethylhexyldiphenyl phosphate and diphenyl hydrogen phosphate.

The preferred phosphates are those where each R is aryl. The most preferred phosphate is triphenyl phosphate. It is also preferred to use triphenyl phosphate in combination with hexabromobenzene and, optionally, antimony oxide.

Also suitable as flame-retardant additives for this invention are compounds containing phosphorus-nitrogen bonds, such as phosphonitrilic chloride, phosphorus ester amides, phosphoric acid amides, phosphonic acid amides, phosphinic acid amides, tris(aziridinyl)phosphine oxide or tetrakis(hydroxy-methyl)phosphonium chloride. These flame-retardant additives are commercially available.

As reinforcing fillers, there may be employed reinforcing amounts of reinforcing filler. In general, any reinforcement can be used, e.g., aluminum, iron or nickel, and non-metals, e.g., carbon filaments, silicates, such as acicular calcium silicate, asbestos, TiO_2, potassium titanate and titanate whiskers, glass flakes and fibers. It is to be understood that, unless the filler adds to the strength and stiffness of the composition, it is only a filler and not a reinforcing filler as contemplated herein. In particular, the reinforcing fillers increase the flexural strength, the flexural modulus, the tensile strength and the heat distortion temperature.

Although it is only necessary to have at least a reinforcing amount of the reinforcement present, in general, the combination of components (a) and (b) will comprise from 10 to 90 parts by weight and the filler will comprise from 10 to 90 parts by weight of the reinforced embodiments of the invention.

In particular, the preferred reinforcing fillers are of glass and it is preferred to use fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively soda free. This is known as "E" glass. However, other glasses are useful where electrical properties are not so important, e.g., the low soda glass known as "C" glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechancial pulling. The preferred filaments for plastics reinforcement are made by mechanical pulling. The filament diameters range from about 0.000112 to 0.00075 inch, but this is not critical to the present invention.

In general, best properties will be obtained if the sized filamentous glass reinforcement comprises from 1 to 80% by weight based on the combined weight of glass and polymers and preferably the glass will comprise from 10 to 40% by weight based on the combined weight of glass and resin. Generally, for direct molding use, up to about 60% of glass can be present without causing flow problems. However, it is useful also to prepare the compositions containing substantially greater

quantities, e.g., up to 70—80% by weight of glass. These concentrates can then be custom blended with blends of resins that are not glass reinforced to provide any desired glass content of a lower value.

The length of the glass filaments and whether or not they are bundled into fibers and the fibers bundled in turn to yarns, ropes or rovings, or woven into mats, are also not critical to the invention. However, in preparing the present compositions it is convenient to use the filamentous glass in the form of chopped strands of from about 1/8" to about 1" long, preferably less than 1/4" long. In articles molded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable, however, because the best properties are exhibited by thermoplastic injection molded articles in which the filament lengths lie between about 0.000005" and 0.125 (1/8").

Because it has been found that certain commonly used flammable sizings on the glass, e.g., destrinized starch or synthetic polymers, contribute flammability often in greater proportion than expected from the amount present, it is preferred to use lightly sized or unsized glass reinforcements in those compositions of the present invention which are flame retardant. Sizings, if present, can readily be removed by heat cleaning or other techniques well known to those skilled in the art.

The manner of combining the ionic copolymer and the linear polyester is not critical; is conventional; and will be obvious to those skilled in the art. These materials as well as any flame retardant, stabilizer, pigment, reinforcement, etc., may be preblended and passed through an extruder or fluxed on a mill at a temperature dependent on the particular composition. The mixed composition can be cooled and cut up into molding granules and molded or extruded or formed into any desired shape. If desired, the composition may be drawn into fiber or films by the use of conventional techniques.

A composition having the following formulation is prepared by melt blending the following materials:

EXAMPLE 1.

	Parts by Weight
Poly(1,4-butylene terephthalate)*	68.8
Ethylene/methacrylic acid copolymer cross-linked with sodium ions**	0.35
Aromatic carbonate copolymer of 50% mol. % of tetrabromobisphenol A and 50% mol. % of bisphenol A (flame retardant)	26.0
Antimony oxide (flame retardant)	5.0

* Having an intrinsic viscosity of about 0.8—1.0 as measured in 60:40 phenol-tetrachloroethane at 30°C.

** Surlyn Ionomer, E.I. duPont de Nemours and Company, No. 1555

This formulation also includes small amounts of conventional antioxidants. After molding, this composition produces pieces which have an average elongation of 255% compared to 16% for a control sample having no ionically cross-linked copolymer. The unusually high elongation value is accompanied by an increase in melt viscosity to 28290 poise[1] from a value of 6440 poise[1] for the control while retaining other critical properties.

If the procedure of Example 1 is repeated, substituting 0.2 and 1.0 wt. % of the ionomer for 0.35 parts by weight, and omitting the flame-retardants, compositions according to this invention will be obtained.

If the procedure of Example 1 is repeated, substituting the following ionomers for the ethylene/methacrylic acid copolymer cross-linked with sodium ions:

ethylene/methacrylic acid (10% conc.) cross-linked with potassium hydroxide;
ethylene/methacrylic acid (10% conc.) cross-linked with lithium hydroxide;
ethylene/methacrylic acid (10% conc.) cross-linked with magnesium acetate;
ethylene/methacrylic acid (10% conc.) cross-linked with aluminum hydroxide;
ethylene/methacrylic acid (10% conc.) cross-linked with nickel acetate;

ethylene/methacrylic acid (10% conc.) cross-linked with cobalt acetate;
ethylene/methacrylic acid (10% conc.) cross-linked with tin acetate;
ethylene/itaconic acid (6% conc.) cross-linked with sodium hydroxide;
ethylene/itaconic acid (6% conc.) cross-linked with strontium hydroxide, compositions according to this invention will be obtained.

If the procedure of Example 1 is repeated, except that 30% by weight of reinforcing fibrous glass filler is included, a reinforced, flame retardant composition according to this invention will be obtained. If the flame retardants are omitted and 30% by weight of reinforcing fibrous glass filler is included, compositions according to this invention will be obtained.

Other modifications and variations of the present invention are possible in the light of the above teachings.

WHAT WE CLAIM IS:—

1. A thermoplastic molding composition which comprises:

(a) a high molecular weight poly(1,4-butylene)terephthalate resin; and

(b) an ionically crosslinked copolymer containing, based on the copolymer weight, at least 50 mol % of residues of α-olefins having the general formula $RCH=CH_2$ where R is hydrogen or an alkyl radical having from 1 to 8 carbon atoms, and 0.2 to 25 mol % of residues of an α,β-ethylenically unsaturated monocarboxylic or dicarboxylic acid, said copolymer containing uniformly distributed throughout a metal ion having a valence of 1 to 3 selected from Na^+, K^+, Li^+, Cs^+, Ag^+, Hg^+, Cu^+, Be^{+2}, Mg^+, Ca^+, Sr^+, Ba^{+2}, Cu^{+2}, Cd^{+2}, Hg^{+2}, Sn^{+2}, Pb^{+2}, Fe^{+2}, Ca^{+2}, Ni^{+2}, Al^{+3}, Se^{+3} Fe^{+3} and Y^{+3}, at least 10 percent of the carboxylic acid groups being neutralized by the said metal ions.

2. A composition as claimed in claim 1 wherein said poly(1,4-butylene)terephthalate resin is poly(1,4-butylene terephthalate).

3. A composition as claimed in claim 1 or claim 2 which includes a reinforcing amount of a reinforcing filler.

4. A composition as claimed in any one of the preceding claims which includes a flame retardant amount of a flame retardant agent.

5. A composition as claimed in any one of the preceding claims wherein said metal ion is Li^+, Na^+ or K^+.

6. A composition as claimed in any one of the preceding claims wherein said at least % of the acid groups of the carboxylic acid monomer are neutralized by said metal ion.

7. A composition as claimed in claim 1 wherein the α-olefin is ethylene, the carboxylic acid monomer is methacrylic acid and the metal ion is sodium.

8. A composition as claimed in claim 1 substantially as hereinbefore described in the Example.

9. A composition as claimed in claim 1 substantially as hereinbefore described.

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